

# FLUORINE GAS GENERATOR

## BACKGROUND OF THE INVENTION

### Field of the Invention

The present invention relates to a fluorine gas generator, in particular a fluorine gas generator capable of generating high-purity fluorine gas having very low impurity content and suited for use in the process of manufacturing semiconductors, among others.

### Description of the Prior Art

Conventionally fluorine gas is one of the key gases essential in the field of semiconductor production, for instance. While it is used as such in certain instances, the demand for nitrogen trifluoride gas (hereinafter referred to as "NF<sub>3</sub> gas") and like gases synthesized based on fluorine gas and intended for use as cleaning gases or dry etching gases in semiconductor manufacturing apparatus has been rapidly increasing. Further, neon fluoride gas (hereinafter referred to as "NeF gas"), argon fluoride gas (hereinafter referred to as "ArF gas"), krypton fluoride gas (hereinafter referred to as "KrF gas") and the like are excimer laser oscillation gases used in patterning of integrated semiconductor circuits, and the raw materials thereof used in many cases are mixed gases composed of a rare gas and fluorine gas.

The fluorine gas or NF<sub>3</sub> gas for use in the manufacture of semiconductors and the like is required to be highly pure with the impurity content as low as possible. On the sites of semiconductor manufacture, for instance, necessary amounts of fluorine gas are taken out of gas cylinders filled with fluorine gas. It thus becomes very important to secure sites for storing such cylinders, store the gas safely, maintain the purity of the gas, and manage for such purposes. As for NF<sub>3</sub> gas, for which the demand has been rapidly increasing lately, the demand tends to exceed the supply, hence there arises a problem that certain amounts of the gas should be in stock. In view of these, to have a fluorine gas generator or producer of the on-demand and on-site type at the site of use thereof is preferred to handling high-pressure fluorine gas cylinders.

Conventionally, fluorine gas is generated in an electrolytic cell such as shown in Fig. 4. Fig. 4 is a schematic representation of a fluorine gas generator. The electrolytic cell body 201 is generally made of Ni, Monel,

carbon steel or the like. Further, at the bottom of the electrolytic cell body 201, a bottom plate 212 made of polytetrafluoroethylene or the like is disposed for preventing the hydrogen gas and fluorine gas generated from being mixed with each other. The electrolytic cell body 201 is filled with an electrolytic bath 202, namely a potassium fluoride-hydrogen fluoride system (hereinafter referred to as "KF-HF system") in the form of a mixed molten salt. The cell or bath is divided into an anode chamber or compartment 210 and a cathode chamber or compartment 211 by means of a skirt 209 made of Monel or the like. Upon applying a voltage between a carbon or nickel (hereinafter referred to as "Ni") anode 203 contained in the anode chamber 210 and a Ni cathode 204 contained in the cathode chamber 211, electrolysis occurs and fluorine gas is generated. The fluorine gas generated is discharged through a product line 208, while the hydrogen gas generated on the cathode side is discharged through a hydrogen gas discharge line 207. In case the electrolytic bath liquid level lowers due to the generation of fluorine gas, hydrogen fluoride (hereinafter referred to as "HF") is directly supplied to the electrolytic bath from an HF feeder 213 connected to an HF feed line extending from outside the electrolytic cell to the electrolytic bath in the cathode chamber. Though not shown, the HF feeding is carried out in association with a sensor for monitoring the electrolytic bath liquid level (cf. e.g. Patent Document 1: Laid-open Japanese Patent Application (JP Kohyo) H09-505853).

However, when HF feeding is stopped in such a fluorine gas generator, the pressure in the HF feed line on the side downstream from a valve disposed on that line becomes negative because of closing of the valve, possibly resulting in flowing in of the electrolytic bath into the HF feed line via the HF feeder 213 and clogging of the line inside due to solidification of the electrolytic bath. The line blocked by the electrolytic bath has to be wholly replaced and, thus, time and cost are required for putting the apparatus back in order.

Furthermore, HF itself is a highly corrosive gas and, for protecting various devices attached to line, the time of their contacting with HF should be as short as possible.

Accordingly, it is an object of the present invention, which has been made in view of the above problems, to provide a fluorine gas generator in which even on the occasion of emergency stop of the fluorine generator or on

the occasion of suspension of HF supply, the electrolytic bath will never enter the upstream line to clog the line inside by solidification or HF will never remain in the line inside.

### SUMMARY OF THE INVENTION

The above object is accomplished by providing, in accordance with the present invention, a fluorine gas generator for generating fluorine gas by electrolyzing an electrolytic bath comprising a hydrogen fluoride-containing mixed molten salt which generator comprises, according to Claim 1, a hydrogen fluoride gas feed line for feeding hydrogen fluoride gas into the electrolytic bath, a first automatic valve disposed on the hydrogen fluoride gas feed line and capable of being closed on the occasion of interruption of feeding of the hydrogen fluoride gas, and an inert gas substitution means for eliminating the hydrogen fluoride gas remaining in the line on the side downstream from the first automatic valve on the hydrogen fluoride gas feed line and substituting an inert gas therefor when feeding of the hydrogen fluoride gas is interrupted.

According to this constitution, after interruption of HF feeding in the fluorine gas generator, an inert gas is substituted for the HF remaining in the line on the side downstream from the first automatic valve on the HF feed line, so that the pressure in the HF feed line will not become negative. Therefore, the electrolytic bath will not enter the HF feed line, hence the clogging of the line inside due to solidification of the electrolytic bath can be avoided and, after inert gas substitution, the devices disposed on the line can be protected against HF. The inert gas includes, but is not limited to, N<sub>2</sub>, He, Ne, Ar, Kr, Xe (xenon), and Rn (radon).

In an embodiment according to Claim 2, the inert gas substitution means in the fluorine gas generator according to Claim 1 comprises a detecting means for detecting interruption of feeding of the hydrogen fluoride gas, an inert gas feed line for feeding the inert gas to the hydrogen fluoride gas feed line on the side downstream from the first automatic valve, and a second automatic valve disposed on the inert gas feed line and operated (opened or closed) in association with the detecting means to feed the inert gas into the line on the side downstream from the first automatic valve on the hydrogen fluoride gas feed line.

According to this constitution, after interruption of HF feeding in the

fluorine gas generator, the inert gas is automatically substituted for the HF remaining in the line on the side downstream from the first automatic valve on the HF feed line, so that the HF feed line will never become negative. As a result, the electrolytic bath will never enter the HF feed line and, thus, the clogging of the line inside due to solidification of the electrolytic bath can be prevented with certainty and the devices disposed on the line after inert gas substitution can be protected against HF.

In an embodiment according to Claim 3, the inert gas feed line in the fluorine gas generator according to Claim 1 or 2 is provided with an inert gas storage tank for storing the inert gas to be fed.

Owing to the inert gas storage tank disposed in the equipment, this constitution makes it possible to feed the inert gas to the HF feed line under a stable pressure and at a constant rate even when the inert gas feeding from the outside is unstable or stopped.

The fluorine gas generator according to Claim 4 is a fluorine gas generator for generating fluorine gas by electrolyzing an electrolytic bath comprising a hydrogen fluoride-containing mixed molten salt which generator comprises a hydrogen fluoride gas feed line for feeding hydrogen fluoride gas into the electrolytic bath, a first automatic valve disposed on the hydrogen fluoride gas feed line and capable of being closed on the occasion of interruption of feeding of the hydrogen fluoride gas, and an inert gas substitution means for eliminating the hydrogen fluoride gas remaining in the line on the side downstream from the first automatic valve on the hydrogen fluoride gas feed line and substituting an inert gas therefor in case of emergency.

According to this constitution, in case of emergency, for example when an emergency button in the fluorine gas generator is pushed, the inert gas is automatically substituted for the HF remaining in the line on the side downstream from the first automatic valve on the HF feed line, so that the pressure in the HF feed line will not become negative. Therefore, the electrolytic bath will not enter the HF feed line, hence the clogging of the line inside due to solidification of the electrolytic bath can be avoided and, after inert gas substitution, the devices disposed on the line can be effectively protected against HF.

In an embodiment according to Claim 5, the inert gas feed line in the fluorine gas generator according to Claim 4 is provided with an inert gas

storage tank for storing the inert gas to be fed.

Owing to the inert gas storage tank disposed in the equipment, this constitution makes it possible to feed the inert gas to the HF feed line at a stable pressure and at a constant rate even when the inert gas feeding from the outside is interrupted in case of emergency.

### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic representation of the principal elements of the fluorine gas generator according to the present invention.

Fig. 2 is an enlargement of the HF feed line and the surroundings thereof shown in Fig. 2.

Fig. 3 (a), (b) and (c) each is a schematic representation of a modification of the inert gas feed line shown in Fig. 1.

Fig. 4 is a schematic representation of a fluorine gas generator conventional in the art.

In the figures, the reference numerals are as respectively defined herein except for the following: 1 for an electrolytic cell, 2 for an electrolytic bath, 3 for an anode chamber, 4 for a cathode chamber, 5 for a first level sensing means, 6 for a second level sensing means, 7, 8 each standing for an automatic valve, 12 for a warm water heater, 14, 15 each for an HF remover, 16 for a partition wall, 22, 23 each for an outlet port for gas, 24 for an HF feed line, 25 for an HF inlet, 31 to 34 and 84 each for a pressure meter, 51 for an anode, 52 for a cathode, 65, 66 each for a manual valve, 73 for a second automatic valve, 74, 82 each for an automatic valve, 81 for a first automatic valve, 83, 85 each for a flowmeter, 91 for an inert gas feed line, 92 for an inert gas storage tank.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Now, referring to Fig. 1 and Fig. 2, an embodiment of the fluorine gas generator according to the present invention is described.

Fig. 1 is a schematic representation of the principal parts of a fluorine gas generator according to the present invention. In Fig. 1, 1 is an electrolytic cell, 2 is an electrolytic bath consisting of a mixed fused or molten KF-HF system-based salt, 3 is an anode chamber, and 4 is a cathode chamber. 5 is a first level sensing means for detecting the liquid level of the electrolytic bath in the anode chamber, and 6 is a second level sensing means for

detecting the liquid level in the cathode chamber. 22 is an outlet port for the fluorine gas generated from the anode chamber 3, 23 is an outlet port for the hydrogen gas generated from the cathode chamber 4, and 24 is an HF feed line for feeding HF to the electrolytic cell 1. 81 is a first automatic valve disposed on the HF feed line, 82 is an automatic valve disposed on the HF feed line, and 83 is a flowmeter for monitoring the rate of flow of HF passing through the HF feed line 24. The "automatic valve" so referred to herein is a valve operated (opened or closed) via a signal from the outside, for example an electromagnetic valve. 84 is a pressure gauge for measuring the pressure of HF. 91 is an inert gas feed line for feeding an inert gas to the HF feed line 24, 92 is an inert gas storage tank for feeding an inert gas to the inert gas feed line, 73 is a second automatic valve disposed on the inert gas feed line 91, and 74 is an automatic valve disposed on the inert gas feed line 91. 14 is an HF remover for removing the HF from the hydrogen-HF mixed gas discharged from the cathode chamber 4, and 15 is an HF remover for removing the HF from the  $F_2$ -HF mixed gas discharged from the anode chamber 3.

The generator further comprises an HF feeding stop detecting means (detecting means) (not shown) for detecting interruption of HF feeding. The inert gas feed line 91, the inert gas storage tank 92, the second automatic valve 73, the automatic valve 74, and an HF feeding interruption detecting means constitute an inert gas substitution means. The line having the inert gas storage tank 92 and the ordinary inert gas feed line 91 may be disposed separately, or the inert gas storage tank 92 may be disposed on one and the same feed line. Each line is preferably provided with a pressure meter and a pressure reducing valve.

The electrolytic cell 1 is made of such a metal or alloy as Ni, Monel, pure iron or stainless steel. The electrolytic cell 1 is divided into the anode chamber 3 and cathode chamber 4 by means of a partition wall 16 made of Ni or Monel. Within the anode chamber 3, there is disposed the anode 51. In the cathode chamber 4, there is disposed the cathode 52. Preferably used as the anode is a low-polarizable carbon electrode. The cathode is preferably made of Ni or the like. The upper covering 17 of the electrolytic cell 1 has inlets/outlets (not shown) for a purge gas from a gas line (not shown), which are constituent elements of a pressure maintenance means for maintaining the anode chamber 3 inside and cathode chamber 4 inside at atmospheric

pressure, the outlet port 22 for the fluorine gas generated in the anode chamber 3, and the outlet port 23 for the hydrogen gas generated in the cathode chamber 4. These outlet ports 22, 23 each comprises a bent pipe made of a material resistant to fluorine gas, such as stainless steel or Hastelloy, for preventing splashes from the anode chamber 3 and cathode chamber 4 from entering the gas lines. The upper covering 17 is also provided with an HF inlet 25 for introducing HF from the HF feeding line 24 when the level of the electrolytic bath 2 descends, together with the first level sensing means 5 and second level sensing means 6.

Fig. 2 is an enlargement of the HF feed line and the surrounding thereof shown in Fig. 1. The HF feed line 24 is connected to an external HF supply source and extends from that connection site to the site of connection to the HF inlet 25 disposed in the electrolytic cell 1. In the vicinity of the electrolytic cell 1, the HF feed line 24 has, from the upstream side to the downstream side, the first automatic valve 81, the flowmeter 83, the automatic valve 82, and the pressure gauge 84, in that order. The first automatic valve 81 is operated in association with the HF feeding interruption detecting means to interrupt the HF supply to the electrolytic cell 1. The flowmeter 83 monitors the rate of flow of the HF being fed to the electrolytic cell 1 via the HF feed line. When the first liquid level sensing means and second liquid level sensing means detect a drop in liquid level of the electrolytic bath, the automatic valve 82 is operated so as to supply HF to the electrolytic bath. The HF feed line 24 is covered with a temperature adjusting heater for preventing HF from liquefaction.

The inert gas feed line 91 is connected to an inert gas supply source outside the fluorine gas generator and extends from that connection site to the vicinity of the electrolytic cell 1 via the inert gas storage tank 92 and, then, is bifurcated in the vicinity of the electrolytic cell 1. One branch of the bifurcated inert gas feed line 91 is connected to an upstream side site of connection to the HF feed line 24 between the first automatic valve 81 and flowmeter 83 disposed on the HF feed line 24, and the other to a downstream side site of connection to the HF feed line 24 between the automatic valve 82 and pressure gauge 84. The second automatic valve 73 is disposed in the vicinity of the upstream side connection site on the bifurcated inert gas feed line 91. The automatic valve 74 is disposed in the vicinity of the downstream side connection site on the inert gas feed line 91. The inert gas

supply source is always feeding the inert gas to the inert gas storage tank 92, and the inert gas storage tank is always feeding the inert gas to the inert gas feed line 91 stably at a constant pressure.

The inert gas feed line 91 may have not only the constitution mentioned above but also one of such constitutions as shown in Fig. 3. Fig. 3 shows three typical modifications of that feed line. For example, according to the constitution shown in Fig. 3 (a), the second automatic valve 73 and automatic valve 74 are omitted and the feed line is directly connected to the HF feed line 24 at a site on the side downstream from the first automatic valve 81 via a nonreturn valve. In this case, the inert gas is fed only during the period when the pressure on the side downstream of the first automatic valve 81 is lower than the pressure in the inert gas feed line 91. Conversely, when the former pressure is higher, the nonreturn valve prevents backflow of the inert gas to the inert gas feed line 91. According to the constitution shown in Fig. 3 (b), the second automatic valve 73 is disposed in lieu of the nonreturn valve in Fig. 3 (a), and the flowmeter 83 is disposed on the side downstream therefrom. In this case, HF feeding is carried out by the application of pressure to the inside of the HF feed line 24. During HF feeding, the second automatic valve 73 remains closed and, upon interruption of HF feeding, the second automatic valve 73 is opened in association with the flowmeter and the inert gas is substituted for the remaining HF. Further, according to the constitution shown in Fig. 3 (c), the inert gas feed line 91 is connected to the HF feed line 24 on the side downstream from the first automatic valve 81 for continuous feeding of the inert gas and for discharging the HF in the line by introduction of  $N_2$  utilizing a mixing effect. In this case, inert gas feeding is continued even after interruption of HF feeding, whereby the HF remaining in the line is replaced by the inert gas.

Now, the manner of HF feeding to the electrolytic bath during ordinary operation of the fluorine gas generator according to the above embodiment is explained. As the electrolysis reaction in the electrolytic bath proceeds, fluorine gas is obtained and at the same time the electrolytic bath is consumed. The consumption of the electrolytic bath is detected by the first level sensing means 5 and second level sensing means 6, which monitor lowering of the electrolytic bath liquid level. When the consumption of a predetermined amount of the electrolytic bath is detected,

an HF feeding operation is effected. Specifically, the second automatic valve 73 disposed on the inert gas feed line 91 connected to the upstream side connection site of the HF feed line 24 is closed, and the first automatic valve 81, the automatic valve 82 and the automatic valve 74 disposed on the inert gas feed line 91 connected to downstream side connection site of the HF feed line 24 are opened. As a result, the inert gas fed from the inert gas storage tank 92 at a constant pressure is fed through the downstream side site of connection between the HF feed line 24 and inert gas feed line 91 to that side of the HF feed line 24 which is downstream from the automatic valve 82. The inert gas fed to the HF feed line 24 serves as a carrier gas and carries HF in the HF feed line to the electrolytic bath. The amount of HF fed to the electrolytic bath is measured by the flowmeter 83.

Upon rising of the electrolytic bath to a predetermined extent as a result of HF feeding, a HF feeding interrupting mechanism detects this through the first level sensing means 5 and second level sensing means 6 and operates to stop HF feeding. Specifically, the first automatic valve 81 is closed to interrupt HF feeding, the automatic valve 82 and second automatic valve 73 are opened, and the automatic valve 74 is closed, whereupon the inert gas fed from the inert gas storage tank 92 at a constant pressure is fed into the HF feed line 24 on the side downstream from the first automatic valve 81 and the HF on the side downstream from the first automatic valve 81 is replaced by the inert gas. As a result, all the HF remaining in the HF feed line 24 can be sent out to the electrolytic cell 1 while the pressure within the line can be maintained. The inert gas now always fed to the electrolytic cell 1 is discharged from the gas outlet 23 together with the hydrogen generated.

Now, the manner of HF feeding to the electrolytic bath of the fluorine gas generator in case of emergency is described. When the fluorine gas generator is in an emergency, HF feeding is stopped by an HF feeding interrupting mechanism. Specifically, the first automatic valve 81 is closed to interrupt HF feeding, the automatic valve 82 and second automatic valve 73 are opened, and the automatic valve 74 is closed. As a result, the inert gas fed from the inert gas storage tank 92 at a constant pressure is fed from the upstream side site of connection between the HF feed line 24 and inert gas feed line 91 into the HF feed line 24 on the side downstream from the first automatic valve 81, and the HF on the side downstream from the first

automatic valve 81 is replaced by the inert gas. Thus, all the HF remaining in the HF feed line 24 can be sent out to the electrolytic cell 1. Even when inert gas feeding from the inert gas supply source is interrupted, the inert gas storage tank 92 contains the inert gas in a sufficient amount for sending out the HF remaining in the HF feed line 24 to the electrolytic cell 1 and for substituting for the HF in that line.

As mentioned above, the fluorine gas generator according to the above embodiment supplies the inert gas to the HF feed line, which gas serves as a carrier gas for HF, and the generator further substitutes the inert gas for the HF in the HF feed line downstream from the closed first automatic valve in case of interruption of HF feeding or in case of emergency.

The fluorine gas generator according to the invention is not limited to the embodiment described above but may include various design modifications, such as ones shown in Fig. 3 (a) to Fig. 3 (c), for instance. Thus, for example, while the second automatic valve 73 is opened in association with the emergency detecting mechanism in the constitution of the above embodiment, the valve 73 may be always opened. According to the latter constitution, only the first automatic valve 81 is to be operated upon interruption of HF feeding, hence the inert gas feed line 91 on the side downstream from branching, the third automatic valve and the automatic valve 74 become unnecessary.

Further, while the inert gas feeding is stabilized by means of the inert gas storage tank 92 in the above embodiment, the generator may have a constitution such that stable inert gas feeding is secured from an external source without using the inert gas storage tank 92.

In case of interruption of HF feeding or in case of emergency in the fluorine gas generator according to the embodiment of the present invention, which has the constitution described above, the first automatic valve 81 is closed, the automatic valve 82 opened, the automatic valve 74 closed, and the second automatic valve 73 opened, and the inert gas is fed into the HF gas feed line 24 on the side downstream from the first automatic valve 81. As a result, even when HF feeding is interrupted, the side downstream from the first automatic valve 81 will not become negative in pressure, hence the electrolytic bath will not flow into the HF gas feed line 24. Further, the time of contact of the flowmeter 83, pressure gauge 84 and other devices disposed on the line with HF can be reduced owing to the state of

substitution of the inert gas for HF except for the periods of HF feeding.

Further, the provision of the inert gas storage tank 92 makes it possible to stably feed the inert gas to the HF feed line 24 even when the inert gas supply from an external source becomes unstable or the supply itself is interrupted.

According to this constitution, even after interruption of HF feeding in the fluorine gas generator, an inert gas is substituted for the HF remaining in the line on the side downstream from the first automatic valve on the HF feed line, so that the pressure in the HF feed line will not become negative. Therefore, the electrolytic bath will not enter the HF feed line, hence the clogging of the line inside due to solidification of the electrolytic bath can be avoided and, after inert gas substitution, the devices disposed on the line can be protected against HF.